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A transformed framework for dynamic correlation in multireference problems

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We describe how multireference dynamic correlation theories can be naturally obtained as single-reference correlation theories in a canonically transformed frame. Such canonically transformed correlation theories are very simple and involve identical expressions to their single-reference counterparts. The corresponding excitations involve quasiparticles rather than the bare particles of the system. High-order density matrices (or their approximations) and the numerical metric instabilities common to multireference correlation theories do not appear. As an example, we formulate the Bogoliubov canonically transformed version of second-order Møller-Plesset perturbation theory and demonstrate its performance in H_2, H_2O, N_2, and BeH_2 bond dissociation. © *2015 AIP Publishing LLC.* [http://dx.doi.org/10.1063/1.4916315]

I. INTRODUCTION

Multireference correlation remains a driving force for the development of new quantum chemical methods. Typically, the orbitals are divided into two sets: an active space with near-degeneracies and an external set of empty or core orbitals. It is now possible to describe the correlation in the active orbitals for active spaces with up to 50 orbitals, to produce a multireference active space wavefunction $|\Psi_0\rangle$ that is formally the sum of many determinants.[1–18] In these cases, the remaining challenge is to efficiently describe the correlation outside of the active space, involving the external orbitals. We refer to this as the dynamic correlation problem in a multireference setting.

Dynamic correlation from a *single* reference (single determinant) can be considered well understood and is well-captured by low-order perturbation theory (such as Møller-Plesset perturbation theory),[19,20] configuration interaction,[19,20] or coupled cluster methods.[21–23] Analogues of these methods for multireference problems, such as multireference perturbation theory,[24–29] multireference configuration interaction,[30–33] and multireference coupled cluster and canonical transformation[34–44] theories have also been formulated. However, all of these multireference formulations are algebraically more opaque and computationally much more expensive than their single-reference counterparts.

Here, we define a natural framework to construct multireference dynamic correlation methods with precisely the same equations and same complexity, as existing well-known and well-understood single-reference theories. The idea is to consider dynamic correlation within the frame of *canonically transformed* interactions and quasiparticles. Within such a view, the multireference initial state is viewed as a "vacuum" of the quasiparticles and the Hamiltonian is expressed in terms of a modified set of "integrals." Once these integrals are defined, the correlation treatment is *precisely* that of a single-reference theory. Thus, complications common to multireference methods, such as high-order density matrices and singular metrics, do not appear. Similar motivations have led to Mukherjee and Kutzelnigg's earlier formulation of the generalized normal ordering and Wick's theorem.[45,46] However, as we shall see, our framework is different, leading to different formalisms or methods. As this paper was finalized for submission, Rolik and Kállay published work[47] with a similar conceptual foundation to our own, although differing in technical details. The relationship between the two is discussed below.

II. RECAP OF CANONICAL TRANSFORMATIONS

We will use the concept of canonical transformations. To improve understanding, we recall some salient points here, and a complete discussion may be found in standard texts.[48,49] We first work with a concrete basis of creation and annihilation operators, c and $c^\dagger$. Any two normalized states are related by a many-particle canonical (i.e., unitary) transformation $\hat{U}$ with $\hat{U}\hat{U}^\dagger = 1$. For example, a multireference state, a sum of many determinants, can be related to a single determinant,

$$|\Psi\rangle = \hat{U}|\mathrm{det}_c\rangle. \tag{1}$$

In Eq. (1), the operator $\hat{U}$ is particle-number-conserving. The transformation may formally be parametrized in exponential form, $\hat{U} = \exp \hat{A}$, where $\hat{A}$ is expanded as

$$\hat{A} = \sum_{pq} A_{pq} c_p^\dagger c_q + \sum_{pqrs} A_{pqrs} c_p^\dagger c_q^\dagger c_r c_s + \cdots, \tag{2}$$

with elements of antihermitian tensors A_{pq}, A_{pqrs}, etc.

A canonical transformation need not be particle-number-conserving. For example, a multireference state can also be related to a vacuum,

$$|\Psi\rangle = \hat{U}|\mathrm{vac}_c\rangle. \tag{3}$$

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In this case, the operator $\hat{A}$ can be written as

$$\begin{aligned}\hat{A} = &\sum_{pq} A_{pq} c_p^\dagger c_q + B_{pq}(c_p^\dagger c_q^\dagger + c_q c_p) \\ &+ \sum_{pqrs} A_{pqrs} c_p^\dagger c_q^\dagger c_r c_s + B_{pqrs}(c_p^\dagger c_q^\dagger c_r^\dagger c_s + c_s^\dagger c_r c_q c_p) \\ &+ \sum_{pqrs} C_{pqrs}(c_p^\dagger c_q^\dagger c_r^\dagger c_s^\dagger + c_s c_r c_q c_p) + \cdots, \end{aligned} \tag{4}$$

where tensors B_{pq}, B_{pqrs}, etc., are also antihermitian. The state $|\mathrm{vac}_c\rangle$ in Eq. (3) is the vacuum of the c operators satisfying the relationship

$$c|\mathrm{vac}_c\rangle = 0 \tag{5}$$

for any c. Particle-number-conserving transformations (1) and (2) are thus a special case of a more general non-number-conserving transformation in Eqs. (3) and (4). We can therefore denote both transformations as $\hat{U}$, without a loss of generality. Note though that an exponential parametrization is *not essential* to the definition of $\hat{U}$. In fact, we do not use such a parametrization in our numerical work below.

Having introduced the concept of a canonical transformation for a multireference state $|\Psi\rangle$, we now discuss canonical transformations with respect to the individual creation and annihilation operators (e.g., c and $c^\dagger$). Let us first consider the case of the number-conserving canonical transformation $\hat{U}$ in Eq. (1). We recall that a single determinant can be expressed as a polynomial of creation operators acting on an appropriate vacuum, i.e., $|\mathrm{det_c}\rangle = c_1^\dagger c_2^\dagger \ldots c_N^\dagger |\mathrm{vac}_c\rangle$. The multireference state $|\Psi\rangle$ can now be written in the following form:

$$\begin{aligned} |\Psi(c,c^\dagger)\rangle &= \hat{U}|\mathrm{det}_c\rangle \\ &= \hat{U} c_1^\dagger \hat{U}^\dagger \hat{U} c_2^\dagger \ldots c_N^\dagger \hat{U}^\dagger \hat{U} |\mathrm{vac}_c\rangle \\ &= a_1^\dagger a_2^\dagger \ldots a_N^\dagger \hat{U}|\mathrm{vac}_c\rangle \\ &= a_1^\dagger a_2^\dagger \ldots a_N^\dagger |\mathrm{vac}_a\rangle \\ &\equiv |\mathrm{det}_a\rangle = |\Psi(a,a^\dagger)\rangle. \end{aligned} \tag{6}$$

Equation (6) demonstrates that a multideterminant N-particle state $|\Psi\rangle$ expressed in the frame of c and $c^\dagger$ operators (i.e., as a polynomial of c and $c^\dagger$) can be written as a single determinant in a new $a, a^\dagger$ frame, involving a simple product of $a^\dagger$ operators. Here, the notation $|\Psi(c,c^\dagger)\rangle$, $|\Psi(a,a^\dagger)\rangle$ is used to denote that these are the *same* states, only expressed as different functions of the underlying $c, c^\dagger$ and $a, a^\dagger$ bases. The notation $|\mathrm{vac}_c\rangle$, $|\mathrm{vac}_a\rangle$ however denotes that the vacua of $c, c^\dagger$ and $a, a^\dagger$ operators are *different*, as they are related by $\hat{U}$.

In Eq. (6), the canonically transformed quasiparticle operators $a, a^\dagger$ are defined as[49,50]

$$a^{(\dagger)} = \hat{U} c^{(\dagger)} \hat{U}^\dagger, \tag{7}$$

where $a^{(\dagger)}$ represents either $a^\dagger$ or a. Since $\hat{U}\hat{U}^\dagger = 1$, the operators $a^{(\dagger)}$ then have the same commutation properties as those of $c^{(\dagger)}$, e.g.,

$$a_p a_q^\dagger + a_q^\dagger a_p = \delta_{pq}. \tag{8}$$

Analogously, for a more general canonical transformation in Eq. (3), we can regard the general state in the $c, c^\dagger$ frame as the *vacuum* in the $a, a^\dagger$ frame

$$\begin{aligned} |\Psi(c,c^\dagger)\rangle &= \hat{U}|\mathrm{vac}_c\rangle = |\mathrm{vac}_a\rangle, \\ a|\mathrm{vac}_a\rangle &= 0. \end{aligned} \tag{9}$$

The simplest canonical transformation is a single-particle transformation. The special particle-number-conserving case is an orbital rotation, corresponding to $\hat{A} = \sum_{pq} A_{pq} c_p^\dagger c_q$, where the amplitudes A_{pq} are the elements of a matrix $\mathbf{A}$. The quasiparticle operators $a_p^{(\dagger)}$ are then expressed as a linear transformation

$$a_p^{(\dagger)} = \sum_q \alpha_{pq} c_q^{(\dagger)}, \tag{10}$$

where the matrix $\boldsymbol{\alpha} = \exp \mathbf{A}$ and $\boldsymbol{\alpha}\boldsymbol{\alpha}^\dagger = \mathbf{1}$. In spin-restricted form, $\boldsymbol{\alpha}$ is the same for up or down spin. The general single-particle transformation (a Bogoliubov transformation)[51] is not number-conserving, corresponding to the first two terms in Eq. (4). In this case, the quasiparticle operators are given by the general linear transformation

$$a_p = \sum_q \alpha_{pq} c_q + \beta_{pq} c_q^\dagger, \tag{11}$$

where the matrices satisfy $\boldsymbol{\alpha}^\dagger\boldsymbol{\alpha} + \boldsymbol{\beta}^\dagger\boldsymbol{\beta} = \mathbf{1}$ for unitarity. In the spin-restricted form, the Bogoliubov transformation becomes

$$a_p = \sum_q \alpha_{pq} c_q + s_p \beta_{pq} c_{\bar{q}}^\dagger, \tag{12}$$

where $s_p = -1$ or $+1$ for the spin-orbital label p with spin up or down, respectively, p and q have the same spin, and $\bar{p}$ corresponds to p with the opposite spin. Equation (12) can be seen to be spin-restricted because the total spin of the state changes in the same way either by creating a particle of given spin ($c_{\bar{q}}^\dagger$) or destroying a particle of opposite spin (c_q). The corresponding Bogoliubov vacuum $|\mathrm{vac}_a\rangle$ defined by Eq. (11) is equivalent to the famous Bardeen-Cooper-Schrieffer (BCS) state of superconductivity.[52–54] Finally, for an arbitrary canonical transformation, the quasiparticle operators are polynomials in the bare particle operators $c^{(\dagger)}$, thus including cubic and higher terms,

$$\begin{aligned} a_p = &\sum_q \alpha^{(1)}_{pq} c_q + \beta^{(1)}_{pq} c_q^\dagger \\ &+ \sum_{qrs} \alpha^{(2)}_{pqrs} c_q^\dagger c_r c_s + \beta^{(2)}_{pqrs} c_q^\dagger c_r^\dagger c_s + \cdots. \end{aligned} \tag{13}$$

Formally, it is entirely equivalent to work in the $c, c^\dagger$ frame or the $a, a^\dagger$ frame. To transform the computation from the $c, c^\dagger$ frame to the $a, a^\dagger$ frame, we must re-express operators (polynomials of $c, c^\dagger$) and states (polynomials of $c, c^\dagger$ acting on $|\mathrm{vac}_c\rangle$), as corresponding functions of $a, a^\dagger$. Consider starting with the electronic Hamiltonian in the bare basis $c, c^\dagger$,

$$\hat{H}(c,c^\dagger) = \sum_{pq} t_{pq} c_p^\dagger c_q + \frac{1}{4} \sum_{pqrs} v_{pqrs} c_p^\dagger c_q^\dagger c_s c_r, \tag{14}$$

where t_{pq} and v_{pqrs} are the usual one- and antisymmetrized two-electron integrals, respectively. To work in the transformed frame, we rewrite this in terms of $a, a^\dagger$ using the inverse of

Eq. (13), yielding

$$\hat{H}(a,a^\dagger) = \sum_{pq} t_{pq}^{(\dagger,\dagger)} a_p^{(\dagger)} a_q^{(\dagger)} + \sum_{pqrs} v_{pqrs}^{(\dagger,\dagger,\dagger,\dagger)} a_p^{(\dagger)} a_q^{(\dagger)} a_r^{(\dagger)} a_s^{(\dagger)} + \sum_{pqrstu} w_{pqrstu}^{(\dagger,\dagger,\dagger,\dagger,\dagger,\dagger)} a_p^{(\dagger)} a_q^{(\dagger)} a_r^{(\dagger)} a_s^{(\dagger)} a_t^{(\dagger)} a_u^{(\dagger)} + \cdots. \tag{15}$$

Higher-body terms and non-particle-number-conserving terms naturally appear in the case of a general transformation (13), since the r.h.s. of Eq. (13) is both non-linear and non-number-conserving. Note the notation $\hat{H}(a,a^\dagger)$ indicates that it is the *same* Hamiltonian as $H(c,c^\dagger)$, only expressed in terms of different particles. As $a(c,c^\dagger)$ and $c(a,a^\dagger)$ are defined in terms of the α and β coefficients in Eq. (13) and the integrals in Eqs. (14) and (15) are related by these coefficients. For a number-conserving single-particle transformation, this relationship is the standard integral orbital transformation. The expressions for a Bogoliubov transformation are given in the Appendix.

III. MULTIREFERENCE AS SINGLE-REFERENCE IN THE TRANSFORMED FRAME

The basic premise of this work is as follows: we are free to work either with the bare particles $(c,c^\dagger)$ or the quasiparticles $(a,a^\dagger)$, thus we can choose the most convenient representation. In the case of a multireference correlation theory, we typically have a multideterminant reference $|\Psi_0\rangle$ defined in a space of core (doubly occupied) and active orbitals. To describe dynamic correlation, excitations between these sets of orbitals and a set of external (unoccupied) orbitals need to be included. The multideterminantal structure of $|\Psi_0\rangle$ in the $c,c^\dagger$ frame gives rise to complicated expressions for the matrix elements of operators, which include up to n-body reduced density matrices for an n-particle operator.[46] On the other hand, in the transformed $a,a^\dagger$ frame, the reference state $|\Psi_0\rangle$ appears simpler, such as a determinant or a vacuum of quasiparticles (Eq. (6) or (9)), and the corresponding matrix elements of operators have single-reference form. Working in the transformed frame requires a more complicated form of the Hamiltonian $\hat{H}(a,a^\dagger)$ (Eq. (15)). However, once the quasiparticle transformation is performed, all equations for the multireference dynamic correlation theory in the transformed $a,a^\dagger$ frame are identical to the single-reference theory, even though the reference state is a multireference state in terms of the bare $c,c^\dagger$ particles.

This strategy defines a general route to obtain multireference correlation theories in the single-reference form. However, a concrete realization requires the explicit canonical transformation $\hat{U}$ relating $|\Psi_0(c,c^\dagger)\rangle$ to a simpler state. For generality, we restrict ourselves to $\hat{U}$ which define $|\Psi_0(c,c^\dagger)\rangle = |\mathrm{vac}_a\rangle$ as in Eq. (9). (This contains the particle-number-conserving transformations in Eq. (6) as a special case, because a determinant can always be viewed as a Fermi vacuum via the particle-hole transformation.) Determining $\hat{U}$ exactly for a complicated $|\Psi_0(c,c^\dagger)\rangle$, such as a complete active space wavefunction, is of exponential complexity. Thus, we must introduce approximations. We do so by considering approximate canonical transformations corresponding to finite truncations of the polynomial expansion in Eq. (13). Then, it is simple to deduce the α,β coefficients of $\hat{U}$ from the low-order density matrices of the multireference state.

For example, consider the lowest-order non-trivial approximation where we truncate Eq. (13) after $\alpha^{(1)}$ and $\beta^{(1)}$, which corresponds to the Bogoliubov transformation considered in Eq. (11). Together with the normalization condition, $\boldsymbol{\alpha}^\dagger\boldsymbol{\alpha} + \boldsymbol{\beta}^\dagger\boldsymbol{\beta} = \mathbf{1}$, $\alpha^{(1)}$ and $\beta^{(1)}$ are completely determined by the single-particle density matrix of $|\Psi_0\rangle$. To demonstrate this compactly, we work with $c,c^\dagger$ corresponding to the natural orbital basis of $|\Psi_0\rangle$, i.e., $\langle\Psi_0|c_p^\dagger c_q|\Psi_0\rangle = n_p\delta_{pq}$ and consider the diagonal spin-restricted Bogoliubov transformation,

$$\begin{aligned} a_p &= \alpha_p c_p + s_p\beta_p c_{\bar{p}}^\dagger, \\ c_p &= \alpha_p a_p - s_p\beta_p a_{\bar{p}}^\dagger, \end{aligned} \tag{16}$$

where we denoted $\alpha \equiv \alpha^{(1)}$ and $\beta \equiv \beta^{(1)}$. Equating the single-particle density matrices of $|\Psi_0\rangle$ in the $c,c^\dagger$ frame and the $a,a^\dagger$ frame, we obtain

$$\begin{aligned} \langle\Psi_0|c_p^\dagger c_p|\Psi_0\rangle &= n_p \\ &\approx \langle \mathrm{vac}_a|\beta_p^2 a_p a_p^\dagger|\mathrm{vac}_a\rangle = \beta_p^2. \end{aligned} \tag{17}$$

Thus, $\beta_p = \sqrt{n_p}$, and from the normalization condition, $\alpha_p = \sqrt{1-n_p}$. Importantly, Eq. (17) is not an equality, since we truncated polynomial expansion (13), indicating that a complete active space state is *not* precisely a Bogoliubov vacuum/BCS state, even if the two states have the same non-idempotent single-particle density matrix. The approximation in Eq. (17) can be improved by including the higher orders in Eq. (13). For example, we can determine products such as $\beta^{(1)}\alpha^{(2)}$ from the two-particle density matrix of $|\Psi_0\rangle$. Thus, a complete hierarchy of approximate canonical transformations corresponding to the full expansion in Eq. (13) can be obtained order by order.

The quasiparticle operators $a^{(\dagger)}$ acting on the vacuum define natural excitations to incorporate into the correlation theory. We first introduce convenient indicial notation. It is usual to choose a convention where we divide the operators $a^{(\dagger)}$ into 3 classes: (i) fully occupied (core) orbitals with indices i,j, (ii) active orbitals with indices x,y, and (iii) empty (external) orbitals with indices a,b. For the general indices, we continue using p,q,r,s. Correlation theories include excitations of the system between the core, active, and external orbitals. With respect to the quasiparticle vacuum, such excitations correspond to creating even sets of quasiparticles on top of the quasiparticle vacuum $|\mathrm{vac}_a\rangle \equiv |\mathrm{vac}\rangle$, e.g.,

$$|ia\rangle = a_i^\dagger a_a^\dagger|\mathrm{vac}\rangle, \ldots, \tag{18}$$

$$|ijxy\rangle = a_i^\dagger a_j^\dagger a_x^\dagger a_y^\dagger|\mathrm{vac}\rangle, \ldots. \tag{19}$$

Each of the kets generated by these excitations is orthonormal and the correlated wavefunction is

$$|\Psi\rangle = |\mathrm{vac}\rangle + \sum_{ia} C_{ia} a_i^\dagger a_a^\dagger|\mathrm{vac}\rangle + \cdots. \tag{20}$$

The expansion coefficients C are formally determined from solving the Schrödinger equation in the quasiparticle representation, which requires evaluation of the Hamiltonian matrix elements in the basis of quasiparticles (e.g., $\langle ia|\hat{H}(a,a^\dagger)|\mathrm{vac}\rangle$).

As we discussed in Sec. II, the quasiparticle Hamiltonian $\hat{H}(a,a^\dagger)$ (Eq. (15)) can be obtained by transforming the original Hamiltonian $\hat{H}(c,c^\dagger)$ in Eq. (14) using the inverse of polynomial expansion (13). Truncating the polynomial expansion (13) at a low order gives rise to the approximate form of $\hat{H}(a,a^\dagger)$, which has a finite (and usually a relatively small) number of terms. As we will show in Sec. IV, in the case of an active-space multireference wavefunction $|\Psi_0\rangle$, the quasiparticle transformation of the Hamiltonian is non-trivial only in the active space, which is usually a relative small part of the orbital space.

IV. CANONICALLY TRANSFORMED SECOND-ORDER MØLLER-PLESSET PERTURBATION THEORY (CT-MP2)

We now have all that is necessary to define a *multireference* dynamic correlation method with precisely the same form and equations as a *single-reference* correlation method. We refer to these methods as *canonically transformed* correlation methods. As a simple example, we describe canonically transformed Møller-Plesset second-order perturbation theory (CT-MP2), where we truncate the polynomial $a(c,c^\dagger)$ at the level of the restricted Bogoliubov transformation in the natural orbital basis (Eqs. (16) and (17)). Although the Bogoliubov transformation is single-particle in form, it captures essential features of the multireference character of $|\Psi_0\rangle$. Importantly, by construction, it exactly recovers the non-idempotent single-particle density matrix of $|\Psi_0\rangle$ and thus does not require any choice of a "leading determinant" in the multideterminant reference wavefunction. The resulting very simple second-order perturbation theory from this quasiparticle vacuum thus captures some features of a more traditional and complicated multireference theory that works with $|\Psi_0\rangle$ directly.

The Bogoliubov Hamiltonian of interest $\hat{H}(a,a^\dagger)$ contains only up to two-particle (four-index) terms, which we write explicitly after normal ordering as

$$\begin{aligned}\hat{H}(a,a^\dagger) = E_0 &+ \sum_{pq} \tilde{t}_{pq} a_p^\dagger a_q + \tilde{g}_{pq} a_p^\dagger a_q^\dagger \\ &+ \frac{1}{4}\sum_{pqrs} (\tilde{v}_{pqrs} a_p^\dagger a_q^\dagger a_r a_s + \tilde{x}_{pqrs} a_p^\dagger a_q^\dagger a_r^\dagger a_s) \\ &+ \frac{1}{4}\sum_{pqrs} \tilde{w}_{pqrs} a_p^\dagger a_q^\dagger a_r^\dagger a_s^\dagger + h.c. \end{aligned} \quad (21)$$

Equation (21) can be obtained by inserting Bogoliubov transformation (16) into Hamiltonian (14). The matrix elements of $\hat{H}(a,a^\dagger)$ in Eq. (21) can be determined with at most $O(M^4)$ cost (where M is the size of the basis set) and are explicitly shown in the Appendix.

To define the perturbation theory, we choose the zeroth-order Hamiltonian $\hat{H}_0 = \tilde{t}_{pq} a_p^\dagger a_q$ and semicanonicalize $\tilde{t}_{pq} \to e_p \delta_{pq}$. Then, the second-order correlation energy from double excitations is given by the single-reference formula

$$E^{(2)} = -\frac{1}{4}\sum_{pqrs} \frac{\langle pqrs|\hat{H}|\text{vac}\rangle^2}{e_p + e_q + e_r + e_s} = -\frac{1}{4}\sum_{pqrs} \frac{\tilde{w}_{pqrs}^2}{D_{pqrs}}, \quad (22)$$

where we allow indices p,q,r,s run over $ij \to ab$, $ij \to xy$, and $xy \to ab$ excitations. The spin-orbital expressions for $\tilde{t}_{pq}$ and $\tilde{w}_{pqrs}$ are given in the Appendix. Equation (22) reduces to that of the standard MP2 in the single-reference limit. The CT-MP2 denominator $D_{pqrs} = (e_p + e_q + e_r + e_s)$ can only become zero if the underlying reference state $|\text{vac}\rangle$ is unstable, i.e., if at least one of $e_p < 0$. Contributions from single excitations also arise from terms such as $\tilde{g}_{pq} a_p^\dagger a_q^\dagger$ of Eq. (21). We do not include such single excitations, as they vanish in the original theory involving $|\Psi_0\rangle$ (e.g., for an orbital optimized multireference state), but are not strictly zero here only because $|\text{vac}\rangle \approx |\Psi_0\rangle$.

It is instructive to analyze the relationship between CT-MP2 and the standard single-reference MP2 theory. There are several contributions to the summation in Eq. (22). Contributions of excitations from core to external orbitals ($ij \to ab$) are equivalent to those in the single-reference case, since $\alpha_i = 0$, $\beta_i = 1$, $\alpha_a = 1$, $\beta_a = 0$ and the denominator $D_{ijab} = (e_a + e_b + e_i + e_j)$ is the standard MP2 denominator, where the sign change from the more usual $(e_a + e_b - e_i - e_j)$ is due to the particle-hole transformation. Let us now analyze contributions that arise from active orbitals. In particular, we consider energy contributions from active to external orbitals ($xy \to ab$), where x and y are weakly occupied ($n_{x,y} \approx 0$), which involve matrix elements $\tilde{w}_{xyab} = v_{xyab}\beta_x\beta_y$. For small deviations away from the single-reference Fermi vacuum (ϵ), we can write $\alpha_x = \cos(\epsilon_x) = 1 - O(\epsilon_x^2)$ and $\beta_x = \sin(\epsilon_x) = \epsilon_x + O(\epsilon_x^3)$. At order ϵ^0, no contributions to the energy arise, since $\beta_x = 0$. The energy contribution at order ϵ^1 is proportional to $(v_{xyab}\epsilon_x\epsilon_y)^2$ scaled by the denominator $(e_a + e_b + e_x + e_y)$. We see that this is similar to a standard MP2 expression involving the active orbitals as if they are singly occupied, but with the integral contributions rescaled by a term on the order of the orbital occupancy ($\epsilon_x^2 \approx \beta_x^2 = n_x$). Similar analysis can be performed for the strongly occupied active orbitals with $n_{x,y} \approx 1$, where the standard MP2 contributions from $\tilde{w}_{xyab}$ appear at order ϵ^0, while new terms arise at order ϵ^1 due to the deviation from single-reference Fermi vacuum.

V. RESULTS

We now demonstrate results of CT-MP2 for the dissociation of H_2, N_2, symmetric bond stretching of water, as well as the Be + H_2 insertion reaction, relative to full configuration interaction (FCI). We compare the performance of CT-MP2 to that of the conventional MP2 theory and the complete active space second-order perturbation theory (CASPT2). The CT-MP2 total energy was obtained by summing the corresponding complete active space self-consistent field (CASSCF) reference energy and the correlation energy computed via Eq. (22).

For the dissociation of H_2, N_2, and H_2O, CT-MP2 yields continuous potential energy curves (PECs), whereas single-reference MP2 theory diverges at large bond distances (Figs. 1–3). Note that the CT-MP2 correlation energy is evaluated with the same computational cost as that of MP2 (and is therefore *much* less costly than CASPT2), although it does require the initial CASSCF state. CT-MP2 does not perform as well as CASPT2, overestimating the correlation energy at the dissociation limit. This can be traced to the decrease in quality of the Bogoliubov transformed vacuum $|\text{vac}\rangle$ (that lies considerably above the Hartree-Fock determinant in energy) at

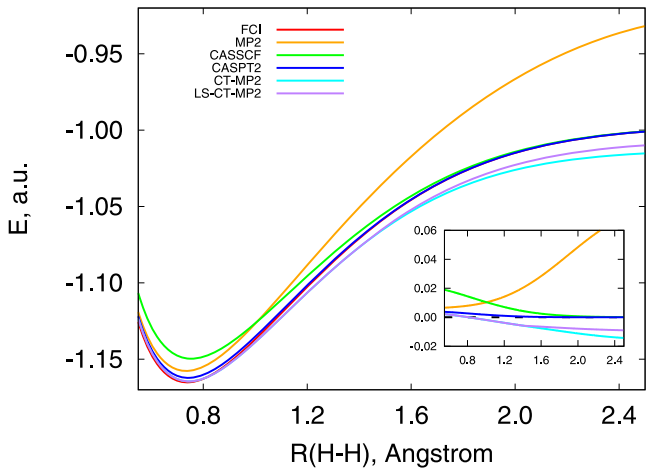

FIG. 1. Total energy as a function of the H_2 bond length (6-31G** basis set). For CASSCF, CASPT2, and CT-MP2, the (2e, 2o) active space was used. For CT-MP2, results obtained with a level shift are also shown, denoted as LS-CT-MP2 (see text for details). The inset shows deviation of the energy from that of FCI.

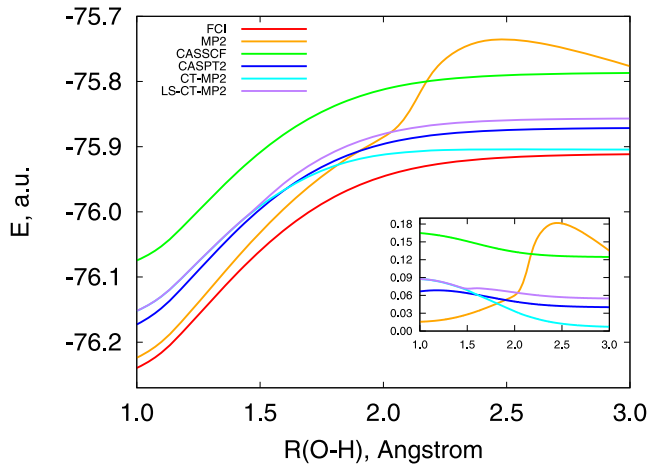

FIG. 3. Total energy as a function of the O–H bond length for the symmetric bond dissociation in water molecule (cc-pVDZ basis set). The H–O–H angle was fixed at 109.57°. For CASSCF, CASPT2, and CT-MP2, the (6e, 5o) active space was used. For CT-MP2, results obtained with a level shift are also shown, denoted as LS-CT-MP2 (see text for details). The inset shows deviation of the energy from that of FCI.

longer distances, which is indicated by the appearance of the negative active-space eigenvalues e_x of the CT-MP2 zeroth-order Hamiltonian. In the case of N_2 dissociation, the poor quality of the quasiparticle vacuum gives rise to an unphysical barrier on the PEC (Figure 2). The errors near dissociation limit can be attributed to the violation of the particle-number symmetry. In principle, this can be easily cured by particle number projection, which converts the Bogoliubov vacuum into an antisymmetrized geminal power.[57–60] Practically, the performance of CT-MP2 at long distances can be improved by adding a level shift to the diagonal part of $\hat{H}_0$, such that no negative eigenvalues appear in Eq. (22).[61] We define the value of the level shift equal to the largest negative eigenvalue of $\hat{H}_0$. In this case, the denominator in Eq. (22) is guaranteed to be non-zero and the correlation energy to have a finite value. Figs. 1–3 show the PECs computed using CT-MP2 with a level shift (denoted as LS-CT-MP2). Applying a level shift results in smooth PECs and reduces the CT-MP2 non-parallelity errors from 96 and 81 mE_h to 30 and 33 mE_h for N_2 and H_2O, respectively (Figures 2 and 3). The LS-CT-MP2 non-parallelity errors are comparable to those of CASPT2 (25 and 27 mE_h for N_2 and H_2O).

In the above examples, we did not observe any intruders in the CT-MP2 calculations. We further tested the performance of CT-MP2 for the insertion of a beryllium atom into H_2 to form BeH_2, a model reaction first studied by Purvis *et al.*[55] Here, we employ a modified variant of the original model,[56] which consists of a beryllium atom placed at the origin of the two-dimensional coordinate system and two hydrogen atoms at positions $y(x) = \pm(2.54 - 0.46x)$. In the range of x from 0 to 4 a_0, the BeH_2 wavefunction changes its ground state electron configuration from that of the linear BeH_2 ($x < 2.5$ a_0, $|\Phi_1\rangle = |(1a_1)^2(2a_1)^2(1b_2)^2\rangle$) to that of the dissociated Be + H_2

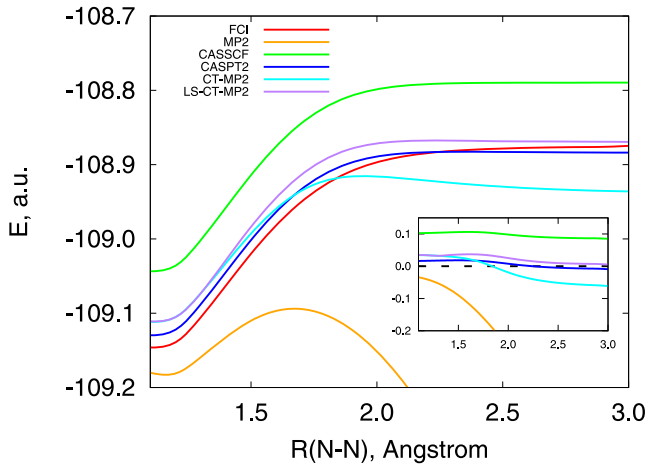

FIG. 2. Total energy as a function of the N_2 bond length (6-311G basis set). For CASSCF, CASPT2, and CT-MP2, the (6e, 6o) active space was used. For CT-MP2, results obtained with a level shift are also shown, denoted as LS-CT-MP2 (see text for details). The inset shows deviation of the energy from that of FCI. FCI energies were obtained by freezing 1s orbitals of nitrogen.

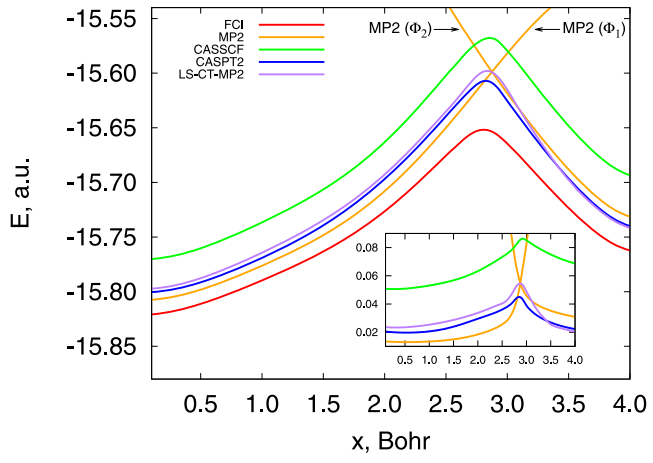

FIG. 4. Potential energy curve for the insertion of a beryllium atom into H_2 (6-311G basis set).[55] A beryllium atom is placed at the origin of the coordinate system, while the positions of the hydrogen atoms are defined as $y(x) = \pm(2.54 - 0.46x)$.[56] For CASSCF, CASPT2, and CT-MP2, the (2e, 2o) active space was used. For CT-MP2, results were obtained with a level shift, denoted as LS-CT-MP2 (see text for details). The inset shows deviation of the energy from that of FCI.

products ($x > 3\ a_0$, $|\Phi_2\rangle = |(1a_1)^2(2a_1)^2(3a_1)^2\rangle$). In a single-reference treatment, one needs to choose a different dominant determinant at different bond lengths, thus one obtains *two* distinct single-reference MP2 energy curves (Figure 4), which cross at $x \approx 2.88\ a_0$. By contrast, although single-reference in complexity, the Bogoliubov vacuum exactly reproduces the non-idempotent density matrix of the superpositions of these two determinants, thus there is only a *single* CT-MP2 curve. Nonetheless, discontinuities in the CT-MP2 curve are observed in the region of $2.6 < x < 3.1\ a_0$. These originate from zero denominators D_{xyab} in Eq. (22) due to the appearance of the negative eigenvalues e_x. In contrast, the level-shifted CT-MP2 (LS-CT-MP2) gives a continuous PEC (Figure 4), which exhibits a non-parallelity error (34 mE_h) comparable to that of CASPT2 (26 mE_h). Thus, the very simple LS-CT-MP2 demonstrates the possibility for a simple perturbation theory, with single-reference cost, to provide qualitatively reasonable PECs for complex bond dissociation. We note, however, that using a level shift is not desirable from a theoretical standpoint, and higher-order canonical transformations need to be explored to avoid it.

VI. FURTHER CONNECTIONS

It is appropriate here to explain the connection of our work with the recent work by Rolik and Kállay in Ref. 47. These authors described a similar strategy to express multireference theories as single-reference theories in terms of quasiparticles. The main conceptual differences lie in the approximate parametrization and determination of $\hat{U}$. First, Rolik and Kállay considered only canonical transformations defined by number-conserving $\hat{U}$. As number-conserving single-particle canonical transformations are trivial orbital rotations, they had to consider canonical transformations involving at least two-particle operators, to describe a non-trivial state (e.g., with a non-idempotent density matrix). However, the simpler general single-particle (Bogoliubov) transformations we used in our calculations above allow any non-idempotent density matrix to be represented, thus capturing multireference behavior at the single-particle level. Second (and more importantly), Rolik and Kállay expressed $\hat{U}$ in exponential form $\hat{U} = \exp \hat{A}$ and determined the amplitudes of $\hat{A}$ from the full configuration interaction coefficients of the multireference state $|\Psi_0\rangle$. This is a procedure with exponential cost. However, as we described above, neither the exponential form nor the full coefficient expansion of $|\Psi_0\rangle$ is necessary to determine the polynomial expansion of $\hat{U}$ to a finite order. Finally, Rolik and Kállay described numerical results for the quasiparticle analogues of coupled cluster theory, while we have focused on perturbation theory.

We further here discuss the connection to the well-known multireference normal ordering introduced by Mukherjee and Kutzelnigg.[46] They defined the multireference normal ordered operator pair $\{c_p^\dagger c_q\} = c_p^\dagger c_q - \gamma_{pq}$, such that $\langle\Psi_0(c,c^\dagger)|\{c_p^\dagger c_q\}|\Psi_0(c,c^\dagger)\rangle = 0$. However, $\{c_p^\dagger c_q\}$ is *not* a pair of quasiparticle operators. Rather,

$$a_p^\dagger a_q = C_0(\alpha,\beta) + C_1(\alpha,\beta)c_p^\dagger c_q + C_2(\alpha,\beta)c_p c_q + C_3(\alpha,\beta)c_p^\dagger c_q^\dagger + C_4(\alpha,\beta)c_p^\dagger c_q^\dagger c_r c_s + \cdots. \quad (23)$$

The Mukherjee-Kutzelnigg formalism arises by truncating after the first two terms and setting $C_1 = 1$, with C_0 being fixed by the vacuum expectation value. However, the general single-particle quasiparticle truncation includes the first four terms. This leads to non-trivial results, as we have seen above.

VII. CONCLUSIONS

In summary, we have formulated a transformation framework to express multireference theories for dynamic correlation in a simple and natural way, similar to that of the single-reference methods. Our approach works in a canonically transformed frame of quasiparticles, equating the quasiparticle vacuum to the multireference state. The canonical transformation can be practically determined from the low-order density matrices of the multireference wavefunction. We demonstrated the theory using a low-order expansion for quasiparticles, corresponding to a Bogoliubov transformation. The corresponding canonically transformed second-order Møller-Plesset perturbation theory has single-reference cost (with no high-order density matrices) but is still able to dissociate multiple bonds, as we demonstrated in the H_2, N_2, H_2O, and BeH_2 molecules. There are many possible extensions of this general framework, and other kinds of multireference dynamic correlation methods can be formulated as canonically transformed versions of the single-reference theories, with exactly the single-reference computational scaling. Further, higher-level polynomial expansions of the quasiparticle operators remain to be explored.

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APPENDIX: BOGOLIUBOV-TRANSFORMED HAMILTONIAN

Here, we present expressions for the matrix elements of Bogoliubov-transformed Hamiltonian (21) derived using the spin-restricted Bogoliubov transformation in the natural spin-orbital basis (Eq. (16)). For the CT-MP2 method, only the $\tilde{t}_{pq}$ and $\tilde{w}_{pqrs}$ matrix elements are necessary to compute the second-order correlation energy in Eq. (22),

$$\begin{aligned}\tilde{t}_{pq} &= (t_{pq} + \sum_r v_{prqr}\beta_r^2)\alpha_p\alpha_q \\ &\quad - (t_{\bar{p}\bar{q}} + \sum_r v_{\bar{p}r\bar{q}r}\beta_r^2)\beta_{\bar{p}}\beta_{\bar{q}}s_{\bar{p}}s_{\bar{q}} \\ &\quad + \frac{1}{2}\sum_r (v_{p\bar{q}\bar{r}r}\alpha_p\beta_{\bar{q}}s_{\bar{q}} + v_{q\bar{p}\bar{r}r}\alpha_q\beta_{\bar{p}}s_{\bar{p}})\alpha_r\beta_{\bar{r}}s_{\bar{r}},\end{aligned} \quad (A1)$$

$$\tilde{w}_{pqrs} = v_{pq\bar{s}\bar{r}}\alpha_p\alpha_q\beta_{\bar{r}}\beta_{\bar{s}}s_{\bar{r}}s_{\bar{s}}. \quad (A2)$$

Note that the matrix elements in Eqs. (A1) and (A2) can be computed with at most $O(M^4)$ scaling, where M is the size of the basis set. Expressions for other matrix elements are shown

below

$$E_0 = \sum_p t_{pp}\beta_p^2 + \frac{1}{2}\sum_{pq} v_{pqpq}\beta_p^2\beta_q^2 + \frac{1}{4}\sum_{pq} v_{p\bar{p}q\bar{q}}\beta_p\alpha_{\bar{p}}\beta_q\alpha_{\bar{q}}s_p s_q, \tag{A3}$$

$$\tilde{g}_{pq} = (t_{p\bar{q}} + \sum_r v_{pr\bar{q}r}\beta_r^2)\alpha_p\beta_{\bar{q}}s_{\bar{q}} + \frac{1}{4}\sum_r (v_{pqr\bar{r}}\alpha_p\alpha_q + v_{\bar{q}\bar{p}r\bar{r}}\beta_{\bar{p}}\beta_{\bar{q}}s_{\bar{p}}s_{\bar{q}})\alpha_{\bar{r}}\beta_r s_r, \tag{A4}$$

$$\tilde{v}_{pqrs} = v_{pqsr}\alpha_p\alpha_q\alpha_r\alpha_s + v_{\bar{p}\bar{q}\bar{s}\bar{r}}\beta_{\bar{p}}\beta_{\bar{q}}\beta_{\bar{r}}\beta_{\bar{s}}s_{\bar{p}}s_{\bar{q}}s_{\bar{r}}s_{\bar{s}} + 4v_{p\bar{r}\bar{q}s}\alpha_p\beta_{\bar{r}}\beta_{\bar{q}}\alpha_s s_{\bar{r}}s_{\bar{q}}, \tag{A5}$$

$$\tilde{x}_{pqrs} = 2v_{pqs\bar{r}}\alpha_p\alpha_q\alpha_s\beta_{\bar{r}}s_{\bar{r}} + 2v_{p\bar{s}\bar{r}\bar{q}}\alpha_p\beta_{\bar{s}}\beta_{\bar{r}}\beta_{\bar{q}}s_{\bar{s}}s_{\bar{r}}s_{\bar{q}}. \tag{A6}$$

The remaining terms in Eq. (21) are Hermitian conjugates of Eqs. (A2), (A4), and (A6). In the single-reference limit, (A1)–(A6) reduce to matrix elements of the standard single-reference normal-ordered Hamiltonian.

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